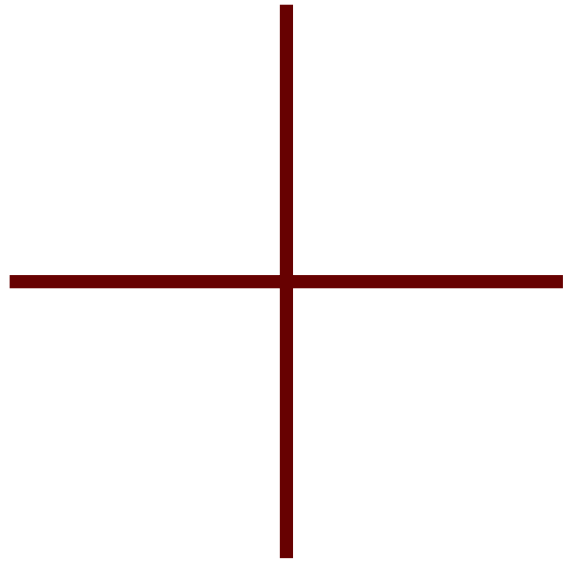


Life Estimation of High Level Waste Tank Steel for F-Tank Farm Closure Performance Assessment



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10/10/2007

Outline

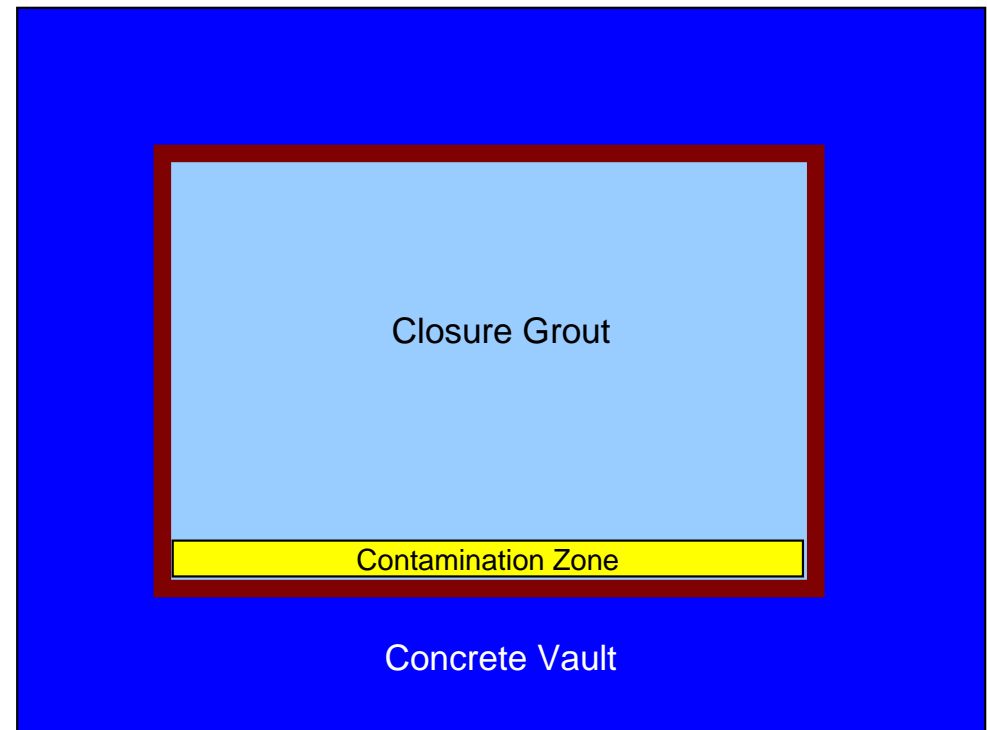
- Performance assessment for tank closure
- Tank life estimation technical approach
 - Deterministic
 - Stochastic
 - Corrosion Mechanisms
- Results
- Recommendations

Tank Closure Performance Assessment

- Performance assessment supporting closure of F-Tank Farm
- Carbon steel of high level waste tank initially provide a barrier contaminant escape
- Corrosion mechanisms will degrade liner over time
- Liner will no longer provide a barrier
- Estimate the time to failure of the tank liner due to corrosion processes

Life Estimate: Deterministic Approach

- Active corrosion mechanisms on the steel under closure conditions
- Assumption of only one liner
- Exposures
 - Contamination Zone
 - Grout/Concrete Vault



Contamination Zone

- Function of the undissolved solids in the residual on tank bottom
- R-value: Ratio of inhibitor species (nitrite and hydroxide) to aggressive species (nitrate + chloride)
 - High R-values: Minimal Corrosion
 - Low R-values High corrosion due to insufficient inhibitors
- Results indicate no accelerated corrosion from contamination zone
- Corrosion rate of 0.04 mils/year (1µm/year) assumed

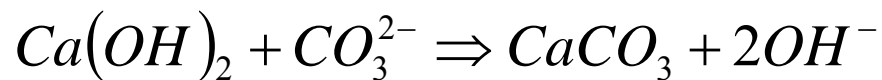
Tank	R-Value
1	5.47
2	4.36
3	3.94
4	9.67
5	5.31
6	12.39
7	3.44
8	3.87
17	3.18
18	4.51
19	0.24
20	3.18
25	3.19
26	3.19
27	3.19
28	3.19
33	4.53
34	12.40
44	4.45
45	3.19
46	3.19
47	3.19

Corrosion in Concrete/Grout

- Corrosion of steel exposed to concrete/grout occurs by a complex mechanism that occurs through metal dissolution at the concrete/metal interface.
- Concrete generally prevents corrosion of the steel
 - Forms passive oxide on the steel surface
 - Maintains a high pH environment
 - Provides a matrix resistant to diffusion of aggressive species
- Passivity can be lost through carbonation or through chloride induced film breakdown
 - Pore water characteristics change with the introduction of chlorides or carbon dioxide, the passive film on the steel may break down

Carbonation

- Pore water pH reduces dramatically due to the conversion of the calcium hydroxide to calcium carbonate through reaction with carbon dioxide



- Complex function of the permeability of the concrete, relative humidity, and the carbon dioxide availability

- Simple Model

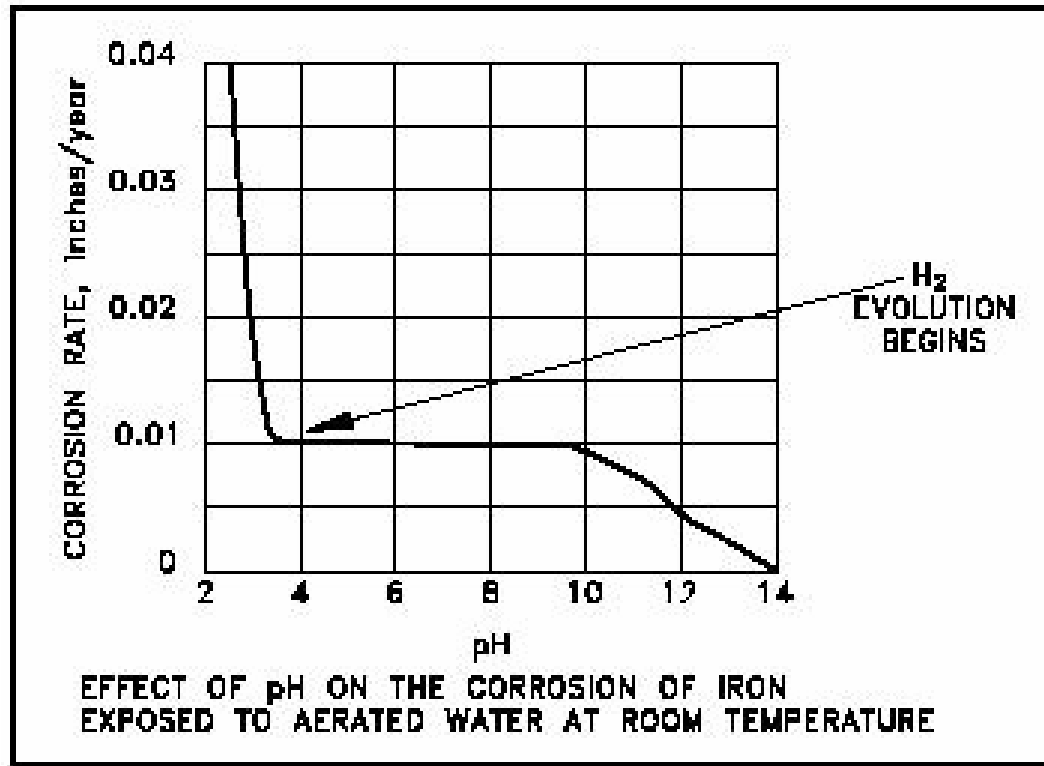
$$X = \left(D_i \frac{C_{gw}}{C_g} t \right)^{\frac{1}{2}}$$

- Assumption: subsurface concrete vaults water saturated
- CO₂ transport is in the aqueous phase.

X	=	carbonation depth (cm)
D _i	=	intrinsic diffusion coefficient of Ca ⁺⁺ in concrete (cm ² /s)
C _{gw}	=	total inorganic carbon in ground water (mole/cm ³)
C _g	=	Ca(OH) ₂ bulk concentration in concrete solid (mole/cm ³)
t	=	time (s)

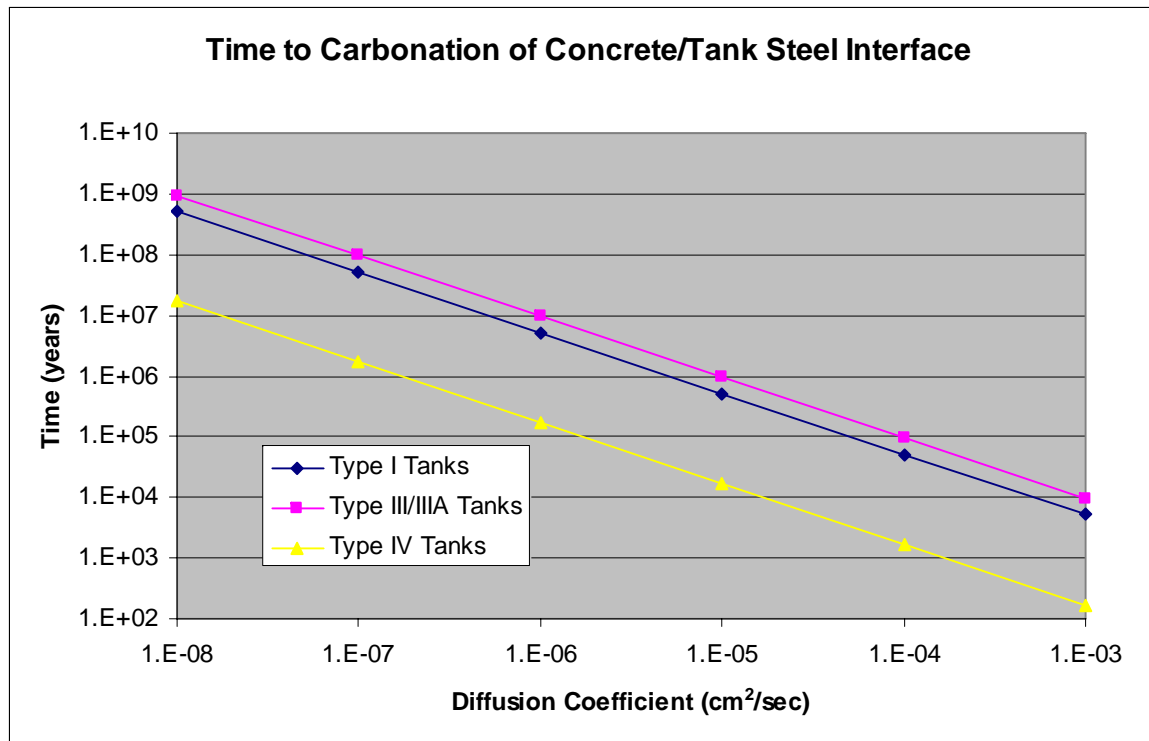
Effect of Carbonation

- Reduction of the pH into a regime where the steel is susceptible to corrosion



Carbonation Times

<u>Parameter</u>	<u>Value</u>
Type I Tank Minimum Concrete Vault Dimension	22-in.
Type III Tank Minimum Concrete Vault Dimension	30-in.
Type IV Tank Minimum Concrete Vault Dimension	4-in.
$D_i (\text{Ca}^{++})$	$1\text{E-}8 \text{ cm}^2/\text{sec} \leq D_i \leq 1\text{E-}3 \text{ cm}^2/\text{sec}$
C_{gw} (as soil moisture content)	$1.93\text{E-}7 \text{ mol}/\text{cm}^3$
C_g	$0.02 \text{ mol}/\text{cm}^3$



Chloride Induced Corrosion: Initiation

- Due to the breakdown of the passive film, thereby indicating that chloride diffusion is the rate controlling step for corrosion initiation
- Followed by oxygen diffusion for corrosion reactions to occur

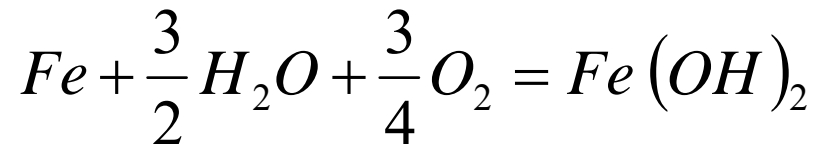
- Simple Empirical Model:

$$t_{initiation} = \frac{129 \cdot t_c^{1.22}}{WCR \cdot [Cl^-]^{0.42}}$$

$t_{initiation}$ = time required for initiation (years)
 t_c = thickness of the concrete cover (in.)
WCR = water-to-cement ratio
[Cl⁻] = chloride concentration in the groundwater (ppm)

Chloride Induced Corrosion: Reaction

- Oxygen diffusion to breakdown of passivity



- Corrosion rate

$$R_{corrosion} = \frac{4}{3} N_{O_2} \frac{M_{Fe}}{\rho_{Fe}}$$

M_{Fe} = molecular weight of iron (56 g/mol)
 ρ_{Fe} = density of iron (7.86 g/cm³)

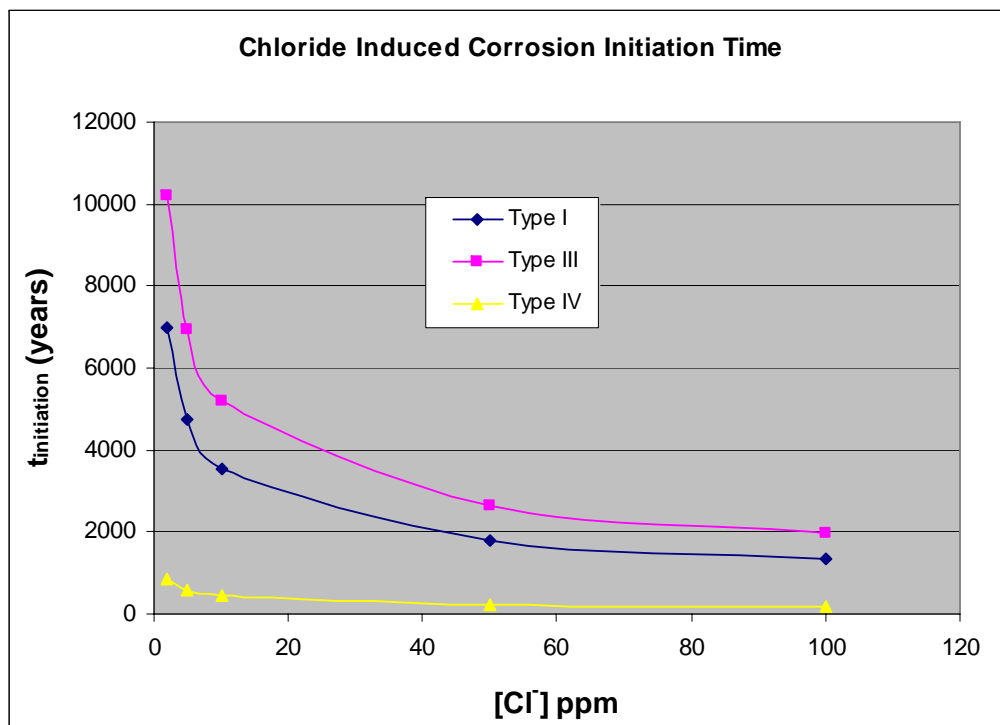
$$N_{O_2} = D_i \frac{C_{gw}}{\Delta X}$$

N_{O_2} = Flux of oxygen through concrete (mol/s/cm²)
 D_i = Oxygen diffusion coefficient in concrete (cm²/sec)
 C_{gw} = Concentration of oxygen in groundwater (mol/cm³)
 ΔX = Depth of concrete (cm)

Chloride Induced Corrosion: Input Parameters

<u>Parameter</u>	<u>Value</u>
Type I Tank Minimum Concrete Vault Dimension	22-in.
Type III Tank Minimum Concrete Vault Dimension	30-in.
Type IV Tank Minimum Concrete Vault Dimension	4-in.
WCR	0.6
[Cl ⁻]	2-100 ppm
D _i (Oxygen)	$1\text{E-}8 \text{ cm}^2/\text{sec} \leq D_i \leq 1\text{E-}3 \text{ cm}^2/\text{sec}$
C _{gw} (Oxygen)	7.25 mg/L

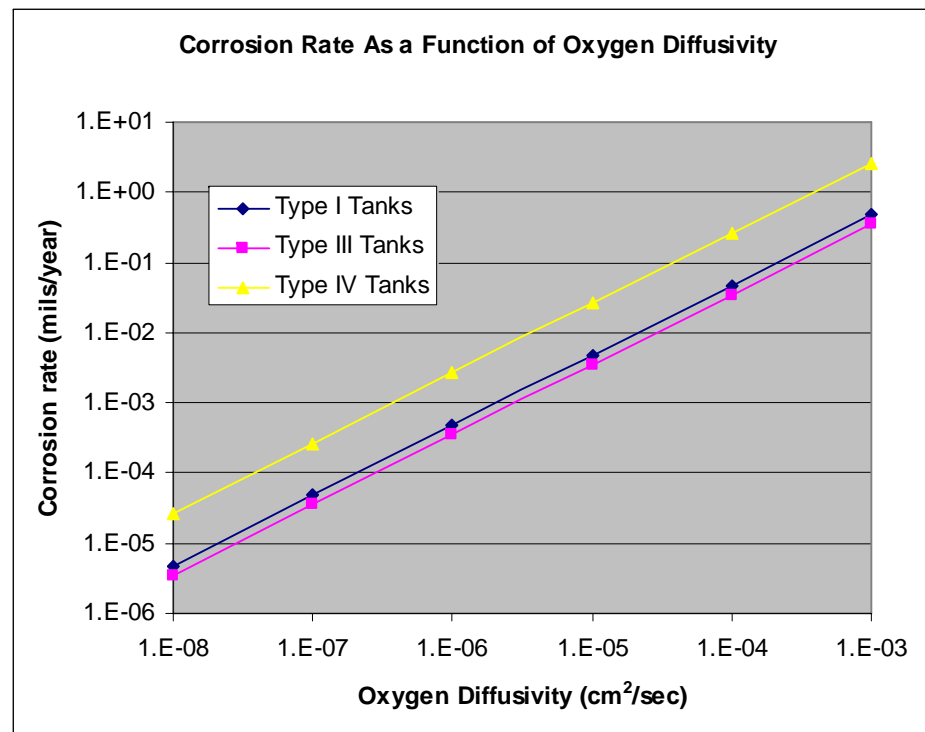
Chloride Induced Corrosion Initiation Time



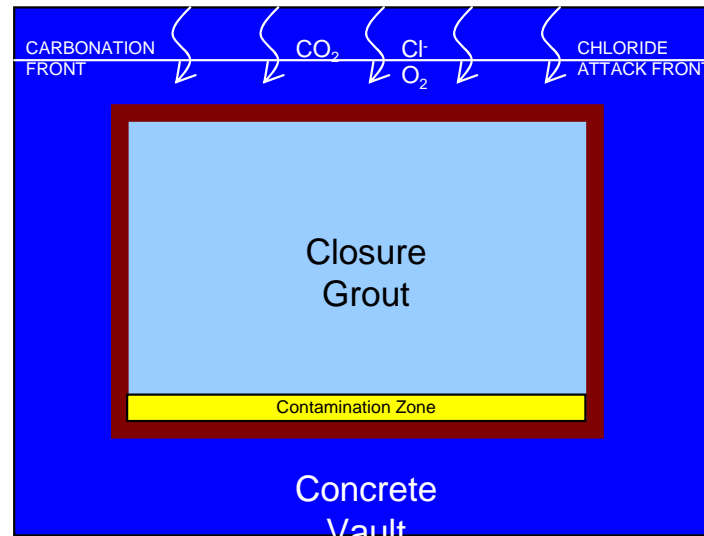
	[Cl ⁻] ppm	t _{initiation} (yrs)
Type I	2	6978
	5	4749
	10	3550
	50	1806
	100	1350
Type III	2	10188
	5	6934
	10	5182
	50	2636
	100	1970
Type IV	2	872
	5	593
	10	444
	50	226
	100	169

Corrosion Rates

- Critical oxygen diffusivity at which the corrosion rate will be greater than 0.04 mils/year corrosion rate:
 - Type I Tank: $8.29 \times 10^{-5} \text{ cm}^2/\text{sec}$
 - Type III Tank: $1 \times 10^{-4} \text{ cm}^2/\text{sec}$
 - Type IV Tank: $1.51 \times 10^{-5} \text{ cm}^2/\text{sec}$



Results of Deterministic Approach

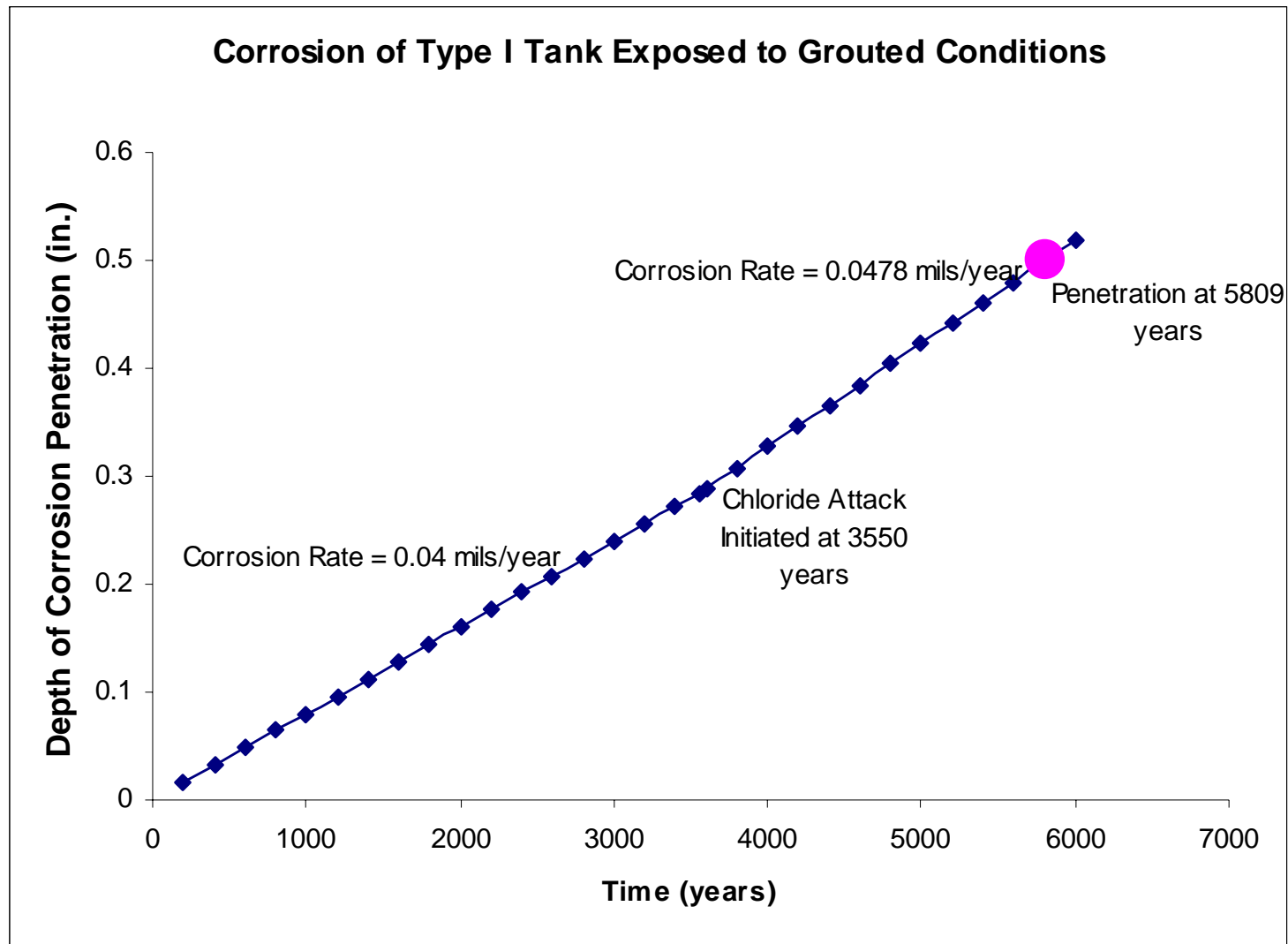


- Initially, general corrosion proceeding at 0.04 mils/year for the tank steel exposed to the concrete/grout.
- Chloride attack then initiated leading to loss of passivity
- Oxygen diffusion for corrosion reactions

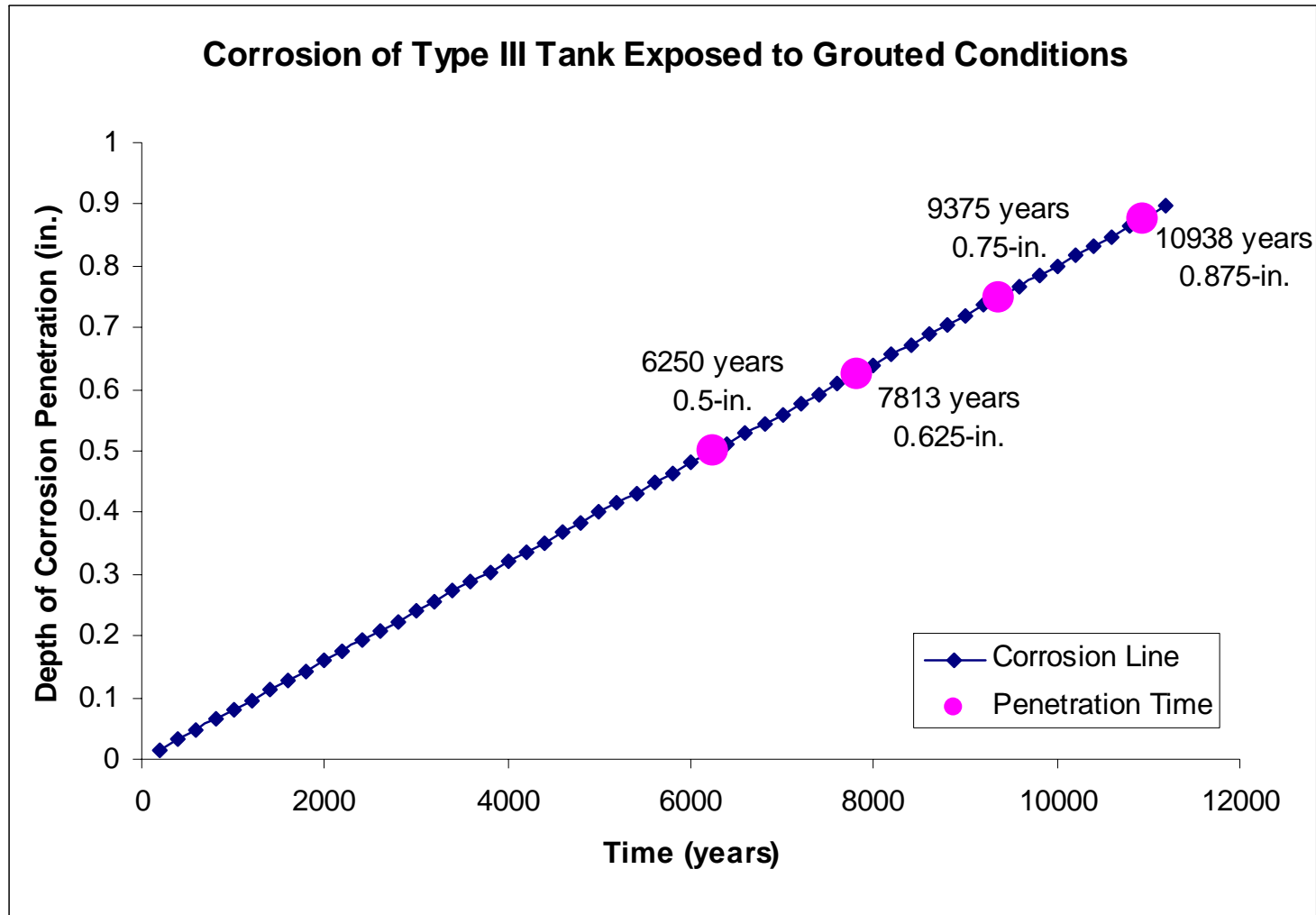
Inputs/Assumptions

- Corrosion is initiated on the both internal and external surfaces of the tank once chloride has penetrated through the thinnest section of concrete.
- Chloride concentration assumed to be 10 ppm
- Oxygen diffusivity is assumed to be $1 \times 10^{-4} \text{ cm}^2/\text{sec}$
- Assume that oxygen is available over the entire surface once the oxygen penetrates the thinnest section of concrete, corresponding to the following corrosion rates:
 - Type I Tanks - 0.0478 mils/year
 - Type III Tanks - 0.04 mils/year
 - Type IV Tanks - 0.26 mils/year

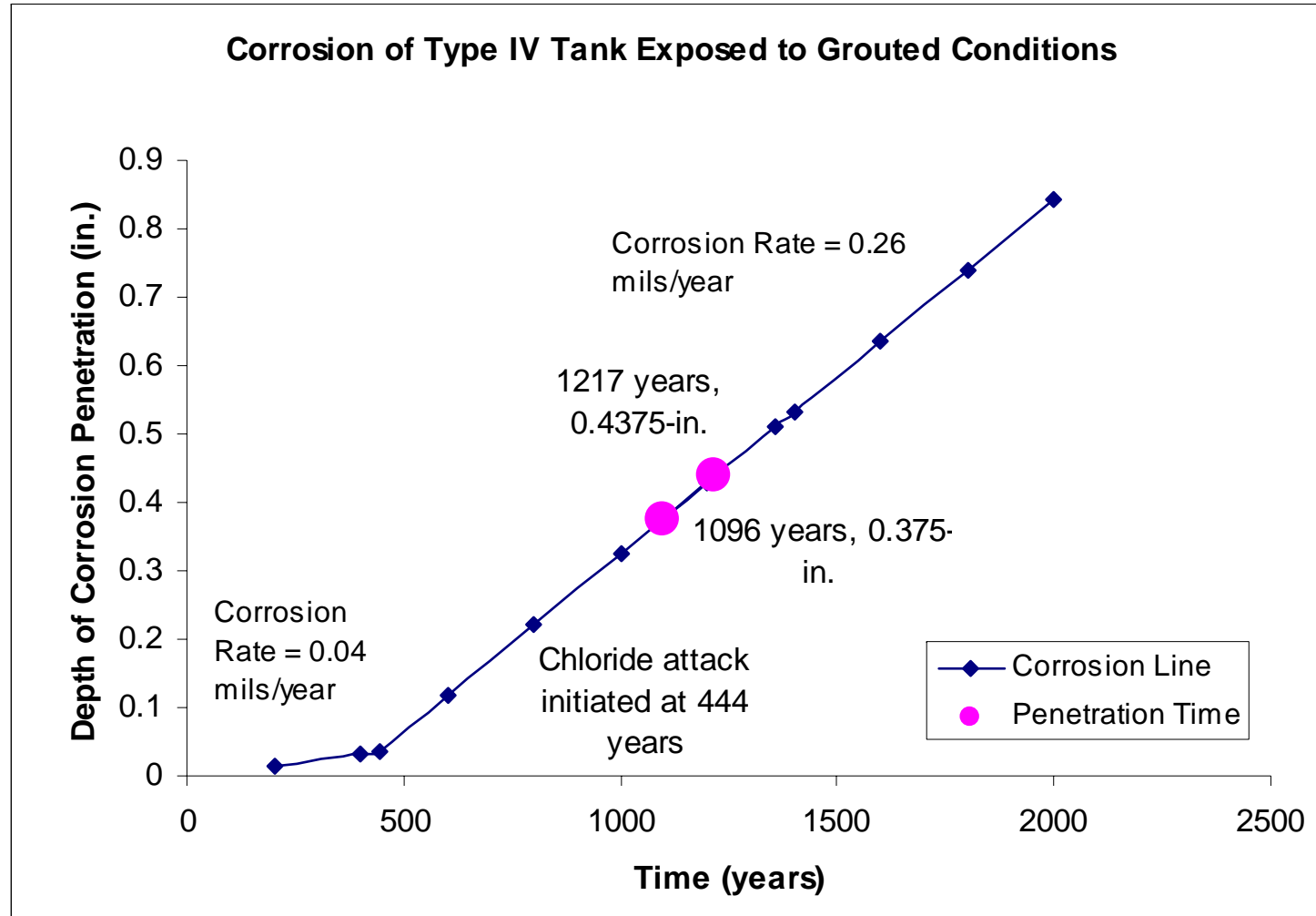
Life Estimation Grouted Conditions: Type I tanks



Life-Estimation Grouted Conditions: Type III Tanks



Life Estimation Grouted Conditions: Type IV Tanks



Life Estimate: Stochastic Approach

- Proposed to account for potential uncertainty in the time-frames proposed for regulatory compliance
- Initially Considered
 - First order reliability methods (FORM)
 - Statistical information is sparse
 - Marginal probability distributions
 - Direct uncertainty analysis
 - Separation of the probability calculations from the evaluation of the performance measure
 - Discretization of the probability intervals
- ***Ultimately, USED Monte Carlo Simulation***
 - Inherently represent the uncertainties in the deterministic approach
 - Large number of simulations
 - Exploits the in-depth knowledge of SRS subsurface environments and HLW tanks as input distributions for the simulations

Stochastic Technical Approach

- Life of the tank liners was assumed to be a function of the time to corrosion initiation plus the time for corrosion to propagate through the liner
- Grouted Conditions
- General corrosion in grouted conditions
- Chloride induced depassivation, followed by general corrosion
- Carbonation induced loss of protective capacity of the concretecombination

$$t_{failure} = t_{initiation} + \frac{Thickness(mils)}{CorrosionRate(mils / year)}$$

$t_{failure}$ = time to complete consumption of the tank wall by general corrosion

$t_{initiation}$ = time to chloride induced depassivation or carbonation front

Thickness = initial thickness of liner (mils)

Corrosion rate:= Dependent upon condition, i.e. chloride or carbonation

Monte Carlo Models

- Case 1: IF $t_{\text{initiation}} [\text{Cl}^-] \geq t_{\text{initiation}} [\text{Carbonation}]$

$$t_{\text{failure}} = t_{\text{initiation}[\text{carbonation}]} + \frac{\text{Thickness}(\text{mils})}{\text{CorrosionRate}(\text{mils} / \text{year})}$$

T_0	=	Initial Thickness (mils)
Thickness	=	$T_0 - 0.04 * t_{\text{init}[\text{carbonation}]} [\text{mils}]$
Corrosion Rate ($R_{\text{carbonation}}$)	=	10 mils/year

- Case 2: IF $t_{\text{initiation}} [\text{Cl}^-] < t_{\text{initiation}} [\text{Carbonation}]$

$$t_{\text{failure}} = t_{\text{initiation}[\text{chloride}]} + \frac{\text{Thickness}(\text{mils})}{\text{CorrosionRate}(\text{mils} / \text{year})}$$

$$R_{\text{corrosion}} = \frac{4}{3} N_{\text{O}_2} \frac{M_{\text{Fe}}}{\rho_{\text{Fe}}}$$

T_0	= Initial Thickness (mils)
Thickness	= $T_0 - 0.04 * t_{\text{init}[\text{chloride}]} [\text{mils}]$
Corrosion Rate ($R_{\text{carbonation}}$)	= calculated

M_{Fe} = molecular weight of iron (56 g/mol)
 ρ_{Fe} = density of iron (7.86 g/cm³)
 N_{O_2} = Flux of oxygen through concrete (mol/s/cm²)

Monte Carlo Models

- Case 3: IF $t_{\text{failure}} [\text{Cl}^-] \geq t_{\text{initiation}} [\text{Carbonation}]$

$$t_{\text{failure}} = t_{\text{initiation}[\text{carbonation}]} + \frac{\text{Thickness(mils)}}{\text{CorrosionRate(mils / year)}}$$

$$T_o - \left[(t_{\text{initiation}[\text{carbonation}]} - t_{\text{initiation}[\text{Cl}]}) \cdot R_{\text{Cl}} + (t_{\text{initiation}[\text{Cl}]} \cdot 0.04) \right]$$

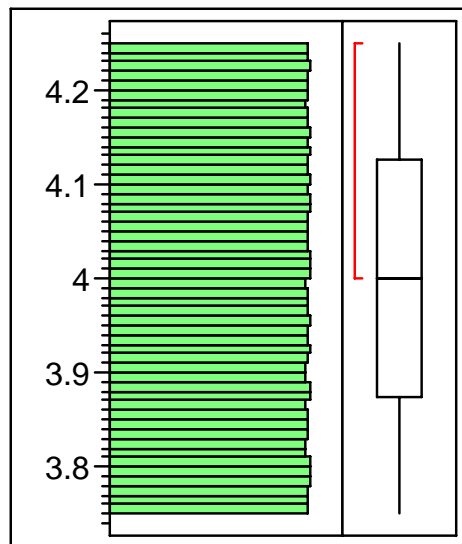
$$t_{\text{failure}} = t_{\text{initiation}[\text{carbonation}]} + \frac{T_o - \left[(t_{\text{initiation}[\text{carbonation}]} - t_{\text{initiation}[\text{Cl}]}) \cdot R_{\text{Cl}} + (t_{\text{initiation}[\text{Cl}]} \cdot 0.04) \right] (\text{mils})}{10(\text{mils / year})}$$

- Chloride induced depassivation → corrosion between initiation time to carbonation and initiation time of chloride induced corrosion → corrosion due to carbonation.

Type IV Tank Simulation: Inputs

Concrete Vault Thickness (in.)

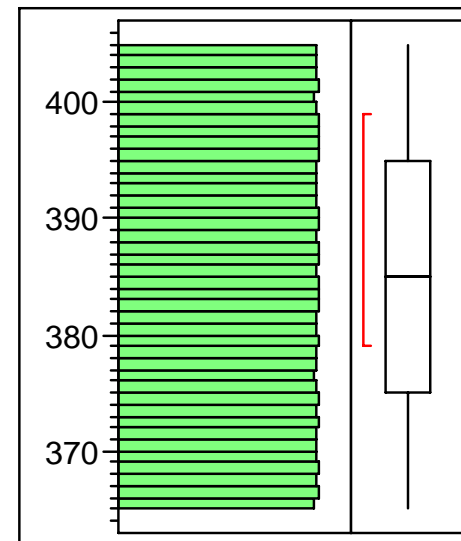
Uniform Distribution



Min:3.75-in.
Median:4-in.
Max:4.25-in
Mean: 4-in.

Steel Liner Thickness (mils)

Uniform Distribution



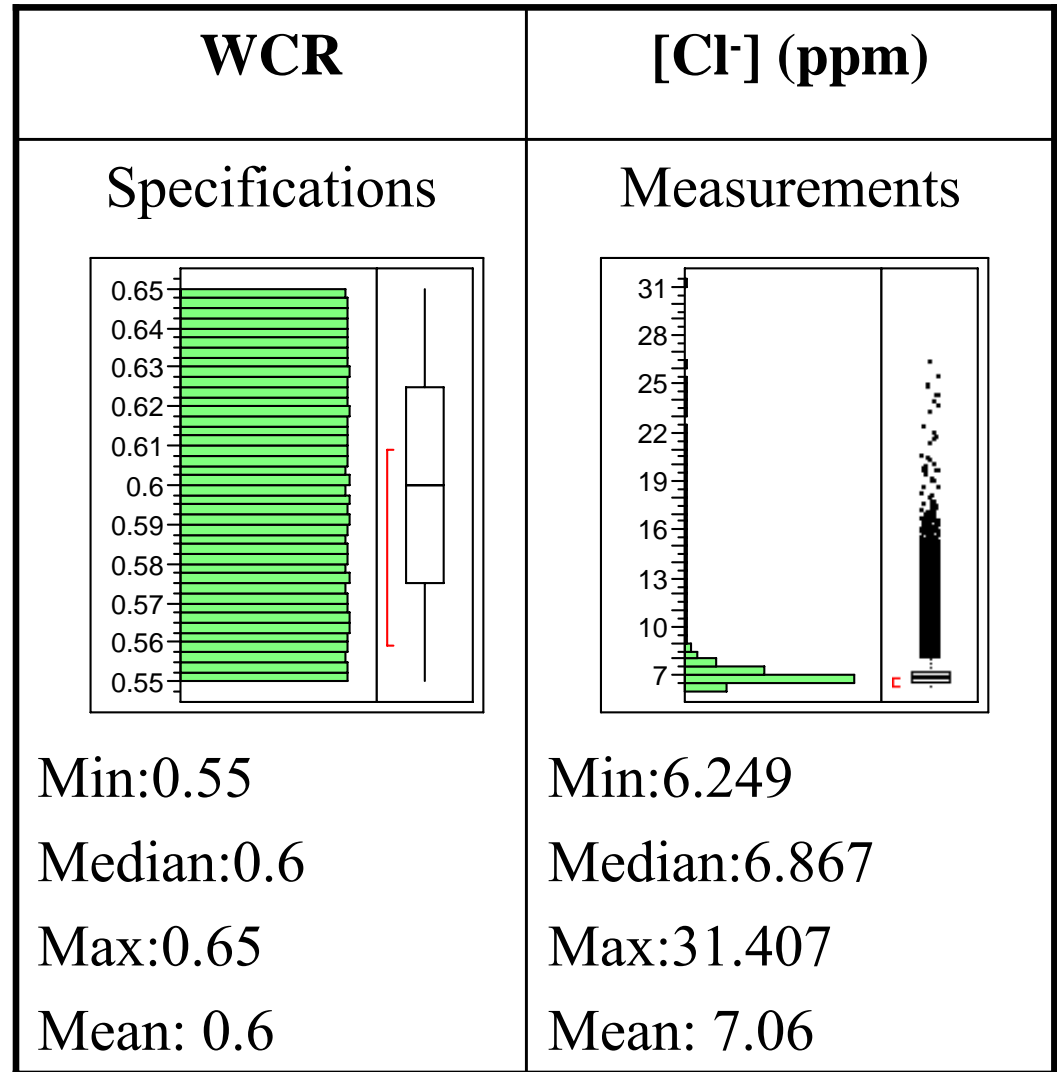
Min:365-mils
Median:385-mils
Max:405-mils
Mean: 385 mils

Initiation of Chloride Attack Input Distributions: Type IV

■ Chloride Initiation

$$t_{\text{initiation}} = \frac{129 \cdot t_c^{1.22}}{WCR \cdot [Cl^-]^{0.42}}$$

$t_{\text{initiation}}$ = time required for initiation (years)
 t_c = thickness of the concrete cover (in.)
 WCR = water-to-cement ratio
 $[Cl^-]$ = chloride concentration in the groundwater (ppm)

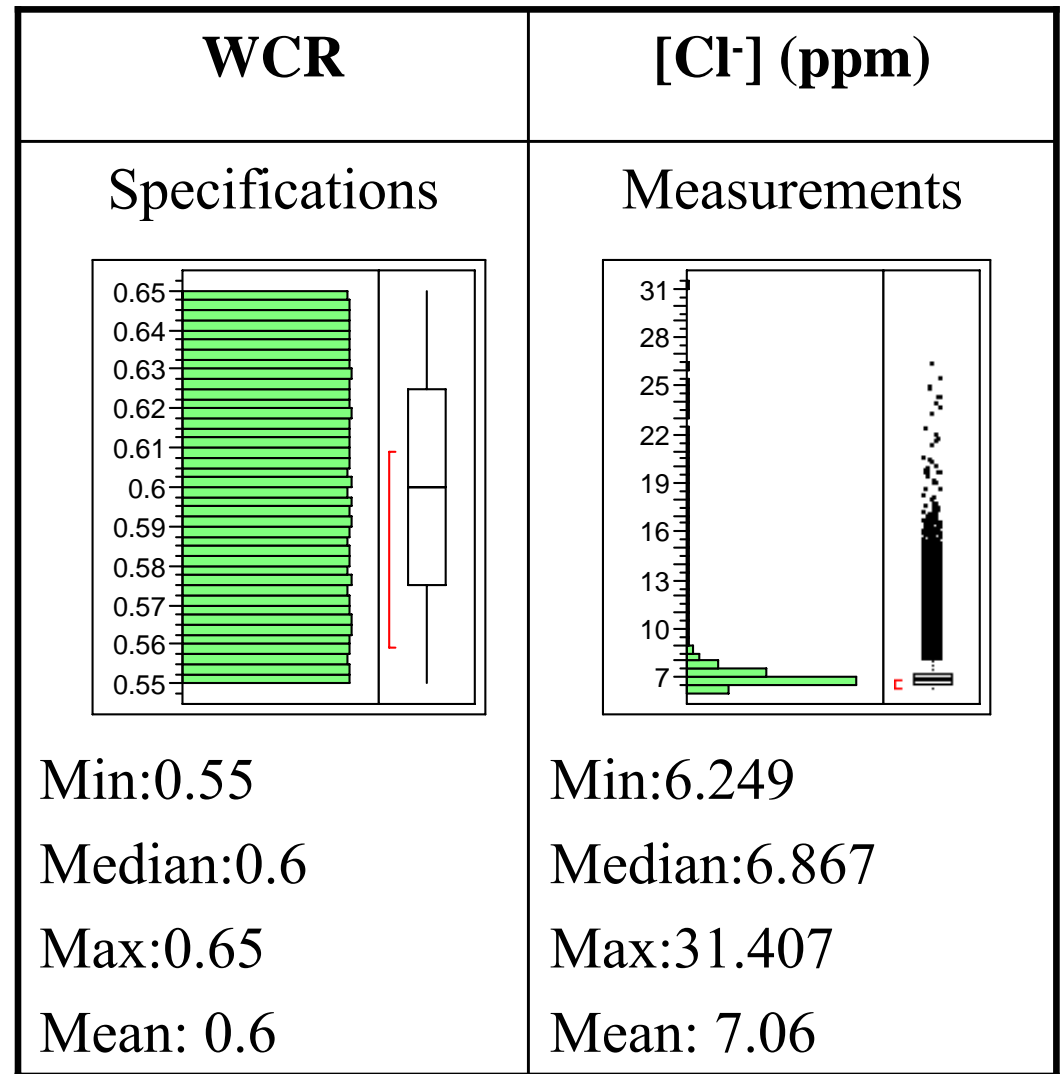


Chloride Corrosion Rate Distributions

■ Chloride Initiation

$$t_{\text{initiation}} = \frac{129 \cdot t_c^{1.22}}{WCR \cdot [Cl^-]^{0.42}}$$

$t_{\text{initiation}}$ = time required for initiation (years)
 t_c = thickness of the concrete cover (in.)
 WCR = water-to-cement ratio
 $[Cl^-]$ = chloride concentration in the groundwater (ppm)

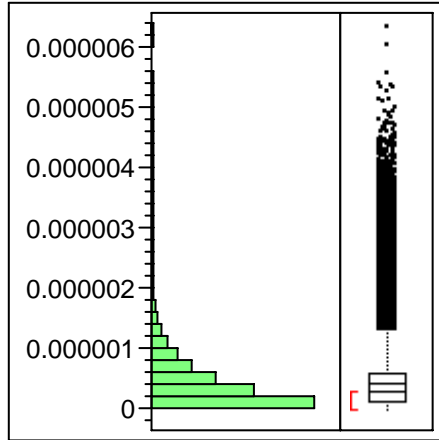
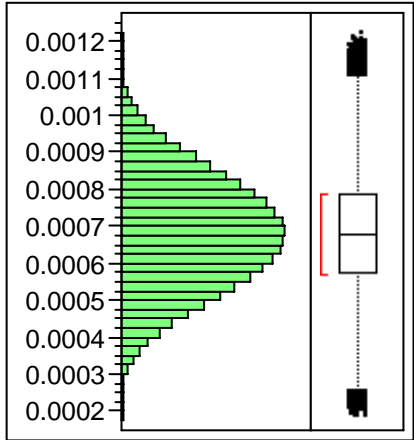


Carbonation Input Distributions: Type IV

■ Carbonation: Simple Model

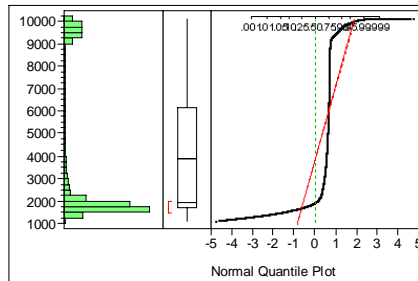
$$X = \left(D_i \frac{C_{gw}}{C_g} t \right)^{\frac{1}{2}}$$

X = carbonation depth (cm)
 D_i = intrinsic diffusion coefficient of Ca^{++} in concrete (cm^2/s)
 C_{gw} = total inorganic carbon in ground water (mole/ cm^3)
 C_g = $\text{Ca}(\text{OH})_2$ bulk concentration in concrete solid (mole/ cm^3)
 t = time (s)

C_{gw} (mol/ cm^3)	$C_g:\text{Ca}(\text{OH})_2$ bulk
<p>Measurements</p>  <p>Min:6.169E-13 Median:3.0338E-7 Max:6.339E-6 Mean: 4.3755E-7</p>	<p>Analytical</p>  <p>Min:0.00019 Median:0.00068 Max:0.0122 Mean: 0.00068</p>

Type IV Results: $D_i(\text{Ca}^{++}) = 1 \times 10^{-8} \text{cm}^2/\text{sec}$, Varied $D_i(\text{O}_2)$

Time to Failure: $D_i(\text{O}_2)=0.0001$



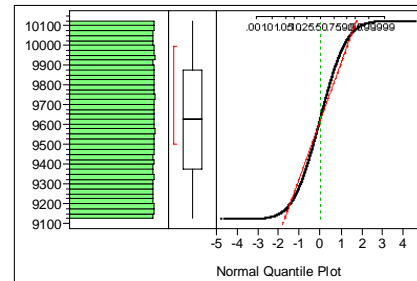
Quantiles

100.0%	maximum	10125
99.5%		10103
97.5%		10014
90.0%		9689
75.0%	quartile	6133
50.0%	median	1920
25.0%	quartile	1678
10.0%		1545
2.5%		1431
0.5%		1346
0.0%	minimum	1110

Moments

Mean	3889.3953
Std Dev	3301.6607
Std Err Mean	3.3016607
upper 95% Mean	3895.8665
lower 95% Mean	3882.9242
N	1000000

Time to Failure: $D_i(\text{O}_2)=0.000001$



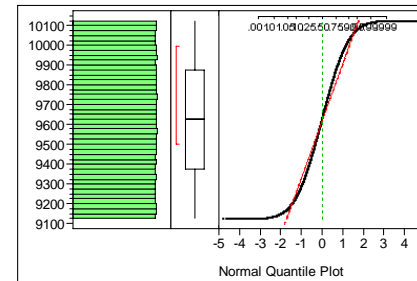
Quantiles

100.0%	maximum	10125
99.5%		10120
97.5%		10100
90.0%		10025
75.0%	quartile	9875
50.0%	median	9626
25.0%	quartile	9376
10.0%		9225
2.5%		9150
0.5%		9130
0.0%	minimum	9125

Moments

Mean	9625.5814
Std Dev	288.30203
Std Err Mean	0.288302
upper 95% Mean	9626.1464
lower 95% Mean	9625.0163
N	1000000

Time to Failure:
 $D_i(\text{O}_2)=0.00000001$



Quantiles

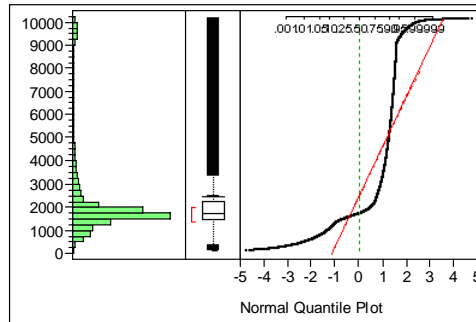
100.0%	maximum	10125
99.5%		10120
97.5%		10100
90.0%		10025
75.0%	quartile	9875
50.0%	median	9626
25.0%	quartile	9376
10.0%		9225
2.5%		9150
0.5%		9130
0.0%	minimum	9125

Moments

Mean	9625.5814
Std Dev	288.30203
Std Err Mean	0.288302
upper 95% Mean	9626.1464
lower 95% Mean	9625.0163
N	1000000

Type IV Results: $D_i(\text{Ca}^{++}) = 1 \times 10^{-6} \text{cm}^2/\text{sec}$, Varied $D_i(\text{O}_2)$

Time to Failure: $D_i(\text{O}_2)=0.0001$



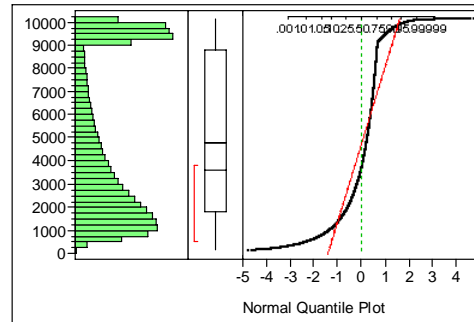
Quantiles

100.0%	maximum	10125
99.5%		10028
97.5%		9656
90.0%		5240
75.0%	quartile	2276
50.0%	median	1754
25.0%	quartile	1509
10.0%		1061
2.5%		654
0.5%		444
0.0%	minimum	152

Moments

Mean	2507.0508
Std Dev	2163.4304
Std Err Mean	2.1634304
upper 95% Mean	2511.291
lower 95% Mean	2502.8105
N	1000000

Time to Failure: $D_i(\text{O}_2)=0.000001$



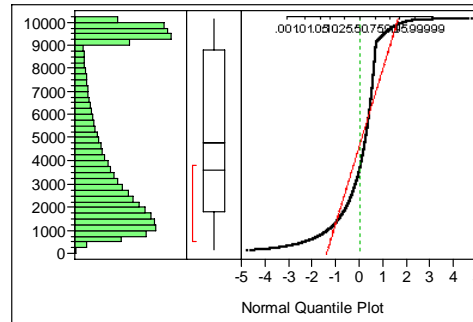
Quantiles

100.0%	maximum	10125
99.5%		10102
97.5%		10012
90.0%		9693
75.0%	quartile	8819
50.0%	median	3638
25.0%	quartile	1805
10.0%		1071
2.5%		655
0.5%		444
0.0%	minimum	152

Moments

Mean	4758.5687
Std Dev	3324.095
Std Err Mean	3.324095
upper 95% Mean	4765.0838
lower 95% Mean	4752.0536
N	1000000

Time to Failure:
 $D_i(\text{O}_2)=0.00000001$



Quantiles

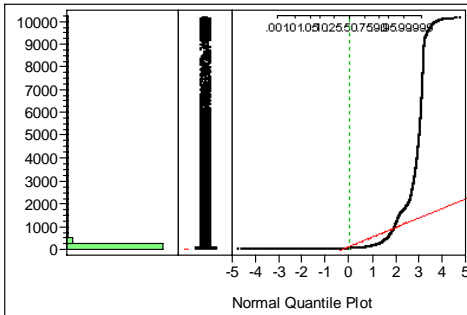
100.0%	maximum	10125
99.5%		10102
97.5%		10012
90.0%		9693
75.0%	quartile	8819
50.0%	median	3638
25.0%	quartile	1805
10.0%		1071
2.5%		655
0.5%		444
0.0%	minimum	152

Moments

Mean	4758.5687
Std Dev	3324.095
Std Err Mean	3.324095
upper 95% Mean	4765.0838
lower 95% Mean	4752.0536
N	1000000

Type IV Results: $D_i(\text{Ca}^{++}) = 1 \times 10^{-4} \text{cm}^2/\text{sec}$, Varied $D_i(\text{O}_2)$

Time to Failure: $D_i(\text{O}_2)=0.0001$



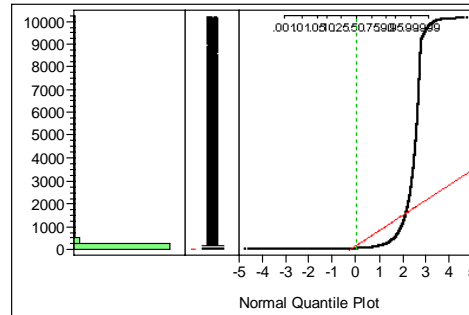
Quantiles

100.0%	maximum	10124
99.5%		2119
97.5%		1041
90.0%		280
75.0%	quartile	126
50.0%	median	75
25.0%	quartile	56
10.0%		49
2.5%		45
0.5%		42
0.0%	minimum	38

Moments

Mean	168.94462
Std Dev	420.1519
Std Err Mean	0.4201519
upper 95% Mean	169.76811
lower 95% Mean	168.12114
N	1000000

Time to Failure: $D_i(\text{O}_2)=0.000001$



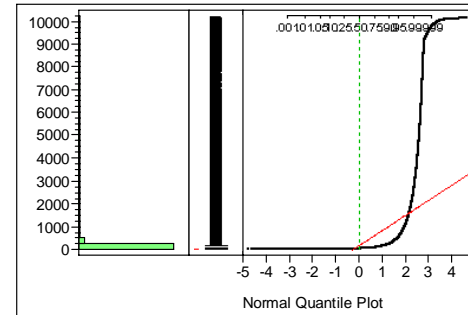
Quantiles

100.0%	maximum	10125
99.5%		5107
97.5%		1050
90.0%		280
75.0%	quartile	126
50.0%	median	75
25.0%	quartile	56
10.0%		49
2.5%		45
0.5%		42
0.0%	minimum	38

Moments

Mean	200.11287
Std Dev	677.54184
Std Err Mean	0.6775418
upper 95% Mean	201.44083
lower 95% Mean	198.78491
N	1000000

Time to Failure:
 $D_i(\text{O}_2)=0.00000001$



Quantiles

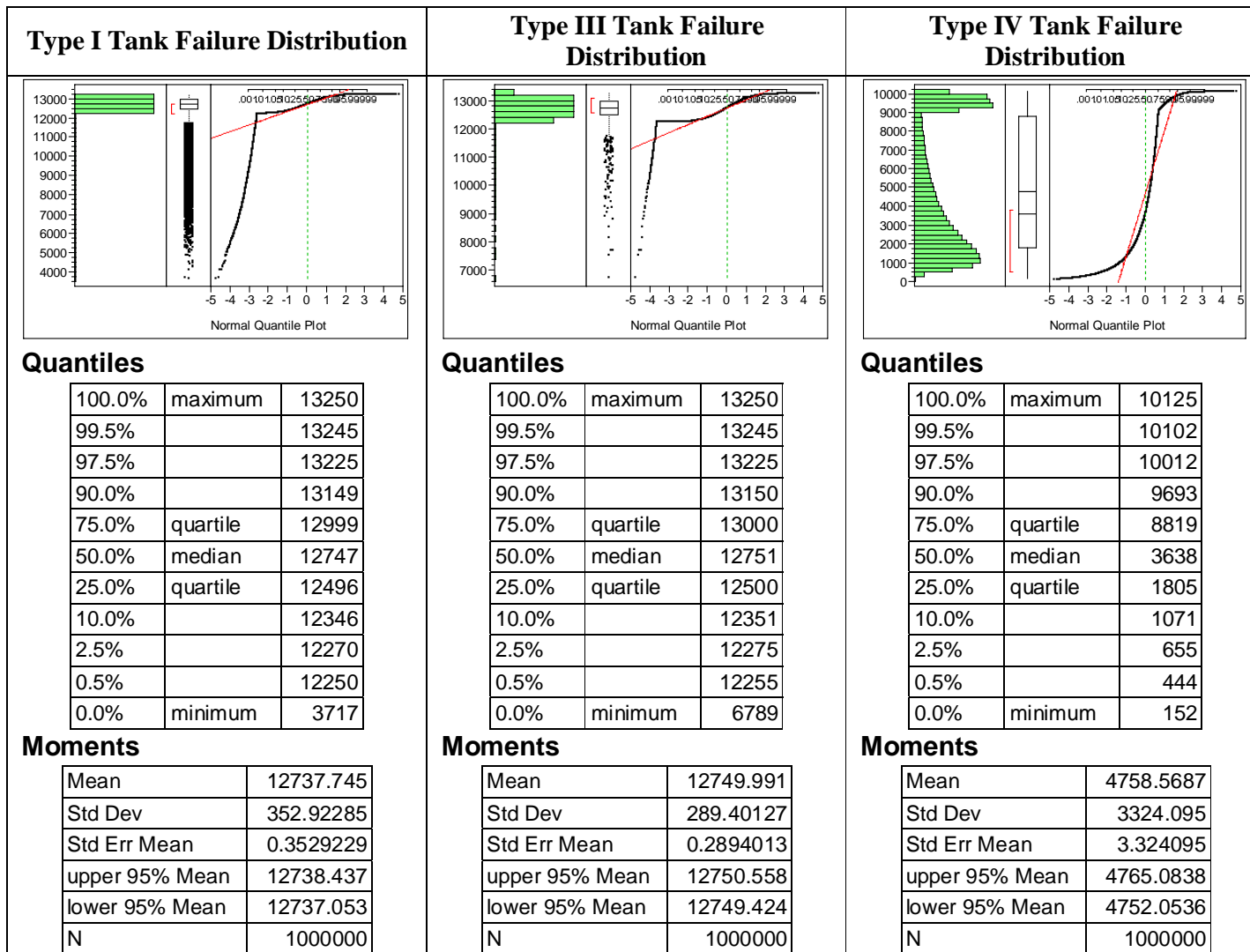
100.0%	maximum	10125
99.5%		5107
97.5%		1050
90.0%		280
75.0%	quartile	126
50.0%	median	75
25.0%	quartile	56
10.0%		49
2.5%		45
0.5%		42
0.0%	minimum	38

Moments

Mean	200.11287
Std Dev	677.54184
Std Err Mean	0.6775418
upper 95% Mean	201.44083
lower 95% Mean	198.78491
N	1000000

Recommendations

- $D_i(\text{Ca}^{2++}) = 1 \times 10^{-6} \text{ cm}^2/\text{sec}$
- $D_i(\text{O}_2) = 1 \times 10^{-6} \text{ cm}^2/\text{sec}$



Summary

- Estimate lifetime of tank steel for performance assessment for tank closure
- Deterministic and Stochastic approaches
- Accounted for corrosion of tank steel liner in contact with grout/concrete
- Data will be used as input into groundwater modeling efforts: PORFLOW and GOLDSIM